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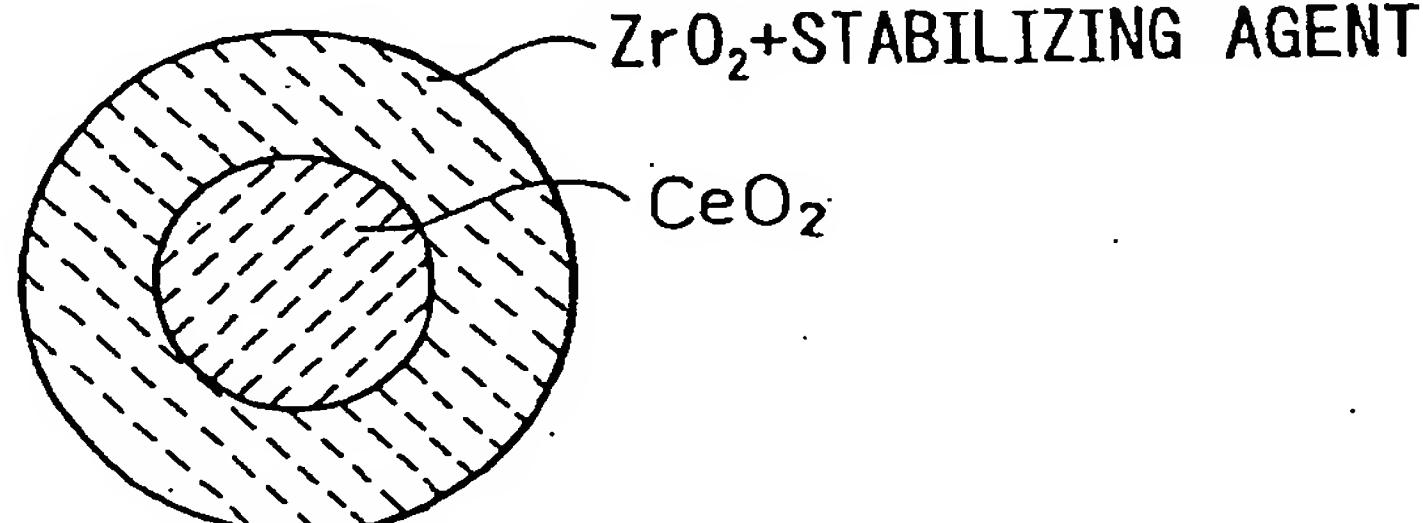
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(54) Cerium-Zirconium composite metal oxide with a cerium oxide core surrounded by zirconium oxide

(57) A cerium-zirconium composite metal oxide having improved durability at high temperature and a stable oxygen storage capacity is provided. The cerium-zirconium composite metal oxide is characterized in that the total mole number of Ce and Zr is at least 85% based on the total mole number of metal in the composite metal oxide, a molar ratio Ce/zr is within a range from 1/9 to 9/1, and an isolectric point of the composite metal oxide is more than 3.5. Preferably, the molar ratio Ce/Zr is

within a range from 3/7 to 7/3 and the isolectric point is within a range from 3.8 to 5.0, and the cerium-zirconium composite metal oxide contains a rare earth metal (excluding Ce) in a concentration of less than 15% by mole based on the total mole number of metal in the composite metal oxide. Also the present invention provides a cerium-zirconium composite metal oxide, characterized in that CeO_2 forms a core surrounded by ZrO_2 .

Fig.1



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Description

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

[0001] The present invention relates to a cerium-zirconium composite metal oxide and, more particularly, to a cerium-zirconium composite metal oxide which is suitable for use as a promoter for an exhaust gas purifying catalyst for an internal combustion engine.

10 2. Description of the Related Art

[0002] Exhaust gas emitted from an internal combustion engine such as an automobile engine includes such substances as nitrogen oxides (NOx), carbon monoxide (CO) and hydrocarbons (HC). These harmful substances can be neutralized by means of a three-way catalyst which oxidizes CO and HC and reduces NOx into O₂.

[0003] Such a three-way catalyst is generally composed of a support made of an oxide such as γ -alumina, and a catalyst component consisting of a noble metal such as platinum (Pt), palladium (Pd) or rhodium (Rh) supported on the support.

[0004] In order for the oxidation of CO and HC and reduction of NOx to proceed efficiently on the three-way catalyst, it is necessary that the air-fuel ratio in the internal combustion engine is properly controlled and that the composition of the exhaust gas lies within a narrow, particular range. In reality, however, the composition of the exhaust gas experiences some variations due to such factor as a delay in the operation of a control system, and may deviate out of the above-mentioned narrow range.

[0005] In a cerium-zirconium composite metal oxide, Ce atoms can change the valence thereof between 3 and 4. In an oxidizing atmosphere including a relatively large amount of O₂ the Ce atom changes the valence from 3 to 4 and absorbs oxygen, while in a reducing atmosphere containing a relatively large amount of CO and HC the Ce atom changes the valence from 4 to 3 and releases oxygen, thus demonstrating an oxygen storage capacity (OSC).

[0006] Therefore, including the cerium-zirconium composite metal oxide in an exhaust gas purifying catalyst has an effect of mitigating the variations in the exhaust gas composition in the vicinity of catalyst component, thereby causing the purification of exhaust gas to proceed more efficiently.

[0007] In addition, absorption of oxygen by the cerium-zirconium composite metal oxide is accompanied by the generation of a significant amount of heat, and the heat can be used to warm up the catalyst when starting up the engine, thus making it possible to shorten the time before the catalyst is activated. For this reason, the cerium-zirconium composite metal oxide is used as a promoter for an exhaust gas purifying catalyst.

[0008] Prior art related to the cerium-zirconium composite metal oxide includes those disclosed in Japanese Unexamined Patent Publication (Kokai) No. 10-194742 and in Japanese Unexamined Patent Publication (Kokai) No. 6-279027.

[0009] However, the cerium-zirconium composite metal oxide has a drawback that the oxygen storage capacity decreases after it has been exposed to a high temperature of about 1000°C or more for a long period of time, thus showing an insufficient durability.

SUMMARY OF THE INVENTION

[0010] Accordingly, an object of the present invention is to provide a cerium-zirconium composite metal oxide having improved durability at high temperature and showing a stable oxygen storage capacity.

[0011] The object described above can be achieved by a cerium-zirconium composite metal oxide characterized in that the total mole number of Ce and Zr is at least 85% based on the total mole number of metal in the composite metal oxide, a molar ratio Ce/Zr is within a range from 1/9 to 9/1, and an isoelectric point of the composite metal oxide is more than 3.5.

[0012] In other word, the present invention provides a cerium-zirconium composite metal oxide which has a specific composition and, especially, has an isoelectric point more than 3.5.

[0013] The term "isoelectric point" is a characteristic value measured on the basis of electrophoresis of particles contained in a slurry, and the isoelectric point of CeO₂ is 2.4 and the isoelectric point of ZrO₂ is 4.0 according to a method specified in the present invention. Accordingly, the cerium-zirconium composite metal oxide of the present invention is characterized in that it has a value of isoelectric point near to that of ZrO₂ while containing both CeO₂ and ZrO₂.

[0014] The cerium-zirconium composite metal oxide of the present invention has a value of the isoelectric point significantly higher than that of the cerium-zirconium composite metal oxide of the prior art which has similar proportions

of CeO_2 and ZrO_2 . An exhaust gas purifying catalyst which has Pt supported on such a cerium-zirconium composite metal oxide has durability significantly improved over that of the prior art.

[0015] Based on these facts, it is considered that the cerium-zirconium composite metal oxide of the present invention has such a constitution as the constituent particles thereof are made mainly of ZrO_2 in the outer layer and mainly of CeO_2 inside, as shown in Fig. 1, and this constitution is stabilized when a trace of element selected from among rare earth metals coexists with ZrO_2 .

[0016] In another aspect, the present invention provides a cerium-zirconium composite metal oxide, characterized in that the total mole number of Ce and Zr is at least 85% based on the total mole number of metal in the composite metal oxide and CeO_2 forms a core surrounded by ZrO_2 .

[0017] When the particles of cerium-zirconium composite metal oxide are made of CeO_2 and ZrO_2 in such a constitution as described above, it is considered that ZrO_2 having high heat resistance maintains the form of particles of cerium-zirconium composite metal oxide so that CeO_2 existing inside and/or CeO_2 - ZrO_2 in the border region between the inside and the outer layer are made stable with time, thereby demonstrating the satisfactory oxygen storage capacity.

[0018] It is to be understood that Fig. 1 shows a mere model and is not intended to limit the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

Fig. 1 shows a model of a cerium-zirconium composite metal oxide of the present invention.

Fig. 2 is a graph showing a relationship between the pH and the zeta potential in the measurement of an isoelectric point.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0020] The present invention provides a cerium-zirconium composite metal oxide, characterized in that the total mole number of Ce and Zr is at least 85% based on the total mole number of metal in the composite metal oxide, a molar ratio Ce/Zr is within a range from 1/9 to 9/1, and an isoelectric point of the composite metal oxide is more than 3.5 and, more preferably, the molar ratio Ce/Zr is within a range from 3/7 to 7/3 and the isoelectric point is within a range from 3.8 to 5.0.

[0021] In the present invention, the isoelectric point is defined as a value measured by the stop watch method, a version of the electrophoretic microscope method specified in JIS R1638.

[0022] The cerium-zirconium composite metal oxide refers to an oxide which contains at least Ce and Zr and may also contain another additional metallic element. The additional metallic element may be selected from among a wide range comprising s-block metals, d-block metals, p-block metals and f-block metals, such as sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), barium (Ba), strontium (Sr), lanthanum (La), yttrium (Y), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), titanium (Ti), tin (Sn), zirconium (Zr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), chromium (Cr), niobium (Nb), copper (Cu), vanadium (V), molybdenum (Mo), tungsten (W), zinc (Zn), aluminum (Al), silicon (Si) and tantalum (Ta).

[0023] The additional metallic element mentioned above is preferably at least one of rare earth metals such as La, Y, Ce, Pr, Nd, Sm, Eu and Gd, and is contained in a concentration less than 15% based on the total mole number of metal in the cerium-zirconium composite metal oxide.

[0024] When such a rare earth metal is used as the additional metallic element, it is considered that ZrO_2 which surrounds the core is especially stabilized.

[0025] The cerium-zirconium composite metal oxide of such a constitution is preferably produced by using a ceria sol as a source of cerium and is obtained by mixing the ceria sol and a zirconium compound solution or a zirconia sol, and preferably a solution of a compound of the additional metallic element or a sol thereof in a predetermined proportion to prepare a suspension, and then drying and firing the suspension.

[0026] The term "sol" in ceria sol and zirconia sol refers to colloid of an oxide or hydrate which is dispersed in a liquid, particularly in water, which can produce a metal oxide such as ceria or zirconia when fired. Specifically, the sol may be a material which is obtained by hydrolyzing alkoxide, acetylacetone, acetate, nitrate or the like of such element as cerium or zirconium in a solution.

[0027] The zirconium compound solution may be, for example, an aqueous solution of zirconium oxynitrate $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, zirconium oxide ZrCl_4 or the like.

[0028] The material is fired, for example, in an air atmosphere at a temperature from 600 to 900°C for several hours. The cerium-zirconium composite metal oxide thus prepared is processed in a grinding process as required, and is provided with a noble metal such as platinum, palladium or rhodium supported thereon, thereby making the exhaust

gas purifying catalyst.

[0029] The exhaust gas purifying catalyst can demonstrate high and stable exhaust gas purifying performance without degradation of the oxygen storage capacity even when exposed to a high temperature of about 1000°C.

[0030] The following Examples further illustrate the present invention.

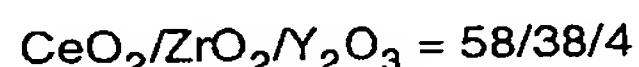
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EXAMPLES

Example 1

10 [0031] A solution prepared by dissolving 41.16 g of zirconium oxynitrate and 6.48 g of yttrium nitrate in 100 g of ion-exchanged water was added to 193.33 g of a ceria sol (containing 15% by weight of Needral U-15, manufactured by TAKI CHEMICAL CO., LTD. as CeO₂) and stirred to prepare a uniform suspension.

15 [0032] The suspension was heated at 120°C for 24 hours to evaporate water, and then fired at 700°C for 5 hours to obtain a cerium-zirconium composite metal oxide of the present invention having the following composition (weight ratio).



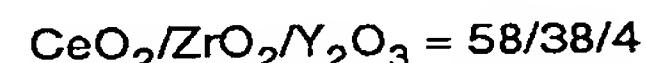
20 [0033] Then, 50 g of this composite metal oxide was dispersed in 300 g of ion-exchanged water to prepare a slurry. Then, 11.36 g of an aqueous solution of a diamminedinitroplatinum complex (Pt concentration: 4.4% by weight) was added to the slurry, followed by stirring for 2 hours.

25 [0034] The slurry was then heated at 120°C for 24 hours to evaporate water, and fired at 500°C for 2 hour to obtain an exhaust gas purifying catalyst comprising a cerium-zirconium composite metal oxide of the present invention and 1% by weight of Pt supported on the cerium-zirconium composite metal oxide.

Example 2

30 [0035] A solution prepared by dissolving 6.48 g of yttrium nitrate in 50 g of ion-exchanged water and 95 g of a zirconia sol (containing 20% by weight of Zirconia HA, manufactured by Daiichi Kigenso Kagaku Kogyo Co., Ltd. as ZrO₂) were added to 193.33 g of the ceria sol described above and stirred to prepare a uniform suspension.

35 [0036] The suspension was heated to evaporate water in the same manner as in Example 1, and then fired at 700°C for 5 hours to obtain a cerium-zirconium composite metal oxide having the following composition (weight ratio) of the present invention.



40 [0037] Then, in the same manner as in Example 1, 1% by weight of Pt was supported on the composite metal oxide using the diamminedinitroplatinum complex to obtain an exhaust gas purifying catalyst of the present invention.

Example 3

45 [0038] A solution prepared by dissolving 6.48 g of yttrium nitrate in 50 g of ion-exchanged water and 154.5 g of a zirconia sol (including 12.5% by weight of Zirconia AC7 manufactured by DAIICHI KIGENSO KAGAKU KOGYO CO., LTD. All as ZrO₂) were added to 193.33 g of the ceria sol described above and stirred to prepare a uniform suspension.

50 [0039] The suspension was heated to evaporate water in the same manner as in Example 1, and then fired at 700°C for 5 hours to obtain a cerium-zirconium composite metal oxide having the following composition (weight ratio) of the present invention.



55 [0040] Then, in the same manner as in Example 1, 1% by weight of Pt was supported on the composite metal oxide using the diamminedinitroplatinum complex to obtain an exhaust gas purifying catalyst of the present invention.

Example 4

[0041] A solution prepared by dissolving 34.66 g of zirconium oxynitrate, 3.99 g of lanthanum nitrate and 8.94 g of praseodymium nitrate in 300 g of ion-exchanged water was added to 193.33 g of the ceria sol described above and then stirred to prepare a uniform suspension.

[0042] The suspension was heated to evaporate water in the same manner as in Example 1, and then fired at 700°C for 5 hours to obtain a cerium-zirconium composite metal oxide having the following composition (weight ratio) of the present invention.

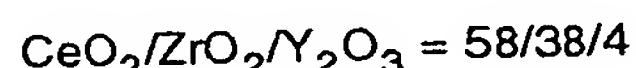


[0043] Then, in the same manner as in Example 1, 1% by weight of Pt was supported on the composite metal oxide using the diamminedinitroplatinum complex to obtain an exhaust gas purifying catalyst of the present invention.

15 Comparative Example 1

[0044] A solution was prepared by dissolving 73.165 g of cerium nitrate, 41.16 g of zirconium oxynitrate and 6.48 g of yttrium nitrate in 500 g of ion-exchanged water. Ammonia water having a concentration of 1 mole/liter was added dropwise to the solution to adjust the pH value to about 9, thereby to obtain a precipitate by coprecipitation.

20 [0045] The solution containing the precipitate was heated to evaporate water in the same manner as in Example 1, and then fired at 700°C for 5 hours to obtain a cerium-zirconium composite metal oxide having the following composition (weight ratio) of the Comparative Example.



[0046] Then, in the same manner as in Example 1, 1% by weight of Pt was supported on the composite metal oxide using the diamminedinitroplatinum complex to obtain an exhaust gas purifying catalyst of the Comparative Example.

30 Comparative Example 2

[0047] A solution was prepared by dissolving 73.17 g of cerium nitrate, 34.66 g of zirconium oxynitrate, 3.99 g of lanthanum nitrate and 8.94 g of praseodymium nitrate in 500 g of ion-exchanged water.

35 [0048] A precipitate was produced from the solution by coprecipitation to evaporate water in the same manner as in Example 1, and then fired at 700°C for 5 hours to obtain a cerium-zirconium composite metal oxide having the following composition (weight ratio) of the Comparative Example.



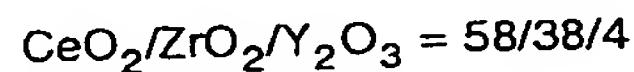
[0049] Then, in the same manner as in Example 1, 1% by weight of Pt was supported on the composite metal oxide using the diamminedinitroplatinum complex to obtain an exhaust gas purifying catalyst of the Comparative Example.

45 Comparative Example 3

[0050] 29 g of cerium oxide powder was dispersed in 500 g of ion-exchanged water, and then a solution prepared by dissolving 41.16 g of zirconium oxynitrate and 6.48 g of yttrium nitrate in 200 g of ion-exchanged water was added dropwise and stirred to prepare a slurry.

50 [0051] Ammonia water was added dropwise to the slurry to adjust the pH value to about 9 in the same manner as in Comparative Example 1 to produce a precipitate containing zirconium and yttrium.

[0052] The slurry was heated to evaporate water, and then fired at 700°C for 5 hours to obtain a cerium-zirconium composite metal oxide having the following composition (weight ratio) of the Comparative Example.



[0053] Then, in the same manner as in Comparative Example 1, 1% by weight of Pt was supported on the composite

metal oxide using the diamminedinitroplatinum complex to obtain an exhaust gas purifying catalyst of the Comparative Example.

Measurement of isoelectric point

[0054] Values of isoelectric point of the samples of cerium-zirconium composite metal oxide produced in Examples 1 to 4 and Comparative Examples 1 to 3 were measured by the stop watch method, a version of the electrophoretic microscope method specified in JIS R1638. The results are summarized in Table 1.

[0055] A relationship between the pH and the zeta potential measured so as to determine the isoelectric point by the measuring method described above for the cerium-zirconium composite metal oxide of Example 1 and Comparative Example 1, CeO_2 powder and ZrO_2 powder are shown in Fig. 2.

[0056] These results show a clear difference in the isoelectric point of the cerium-zirconium composite metal oxide between the Examples and the Comparative Examples. The Examples showed isoelectric points near that of ZrO_2 powder, while the Comparative Examples showed isoelectric points near that of CeO_2 powder.

[0057] As the compositions of the cerium-zirconium composite metal oxide were the same between Examples 1 to 3 and Comparative Examples 1 and 3, and Example 4 and Comparative Example 2, the difference described above is considered to be attributed to the form of CeO_2 and ZrO_2 . It is believed that the Examples showed the isoelectric point near that of ZrO_2 powder since the cores made of CeO_2 are surrounded by ZrO_2 in the Examples as shown in Fig. 1.

Evaluation of catalyst performances

[0058] The samples of cerium-zirconium composite metal oxide made in Examples 1 to 4 and Comparative Examples 1 to 3 were compressed and crushed to make pellets about 2 mm in diameter. About 2.0 g of each of the samples was taken and tested to evaluate catalyst performances.

[0059] The exhaust gas purifying catalysts were fired at 1000°C for 3 hours for the purpose of comparing the durability, before the evaluation of catalyst performances.

[0060] Evaluation test was conducted by measuring the rate of neutralizing the components C_3O_6 (HC), NO and CO while raising the catalyst bed temperature at a rate of 10°C /minute up to 400°C, and changing between carbon rich gas and lean gas having compositions shown in Table 1 at intervals of one minute, so that any difference in the oxygen storage capacity can be observed distinctly. The catalytic performances were evaluated in terms of the temperature at which 50% of the component was neutralized. The test results are summarized in Table 2.

(Table 1)

Gas composition for evaluation								
	N_2 (%)	CO_2 (%)	NO (ppm)	CO (%)	C_3H_6 (ppmC)	H_2 (%)	O_2 (%)	H_2O (%)
Rich gas	Balance	10	2200	2.80	2500	0.27	0.77	10
Lean gas	Balance	10	2200	0.81	2500	0	1.7	10

(Table 2)

Results of the measurement of catalyst performances and isoelectric point						
	Composition	Weight ratio	HC	NO	CO	Isoelectric point
Example 1	Ce-Zr-Y-O	58/38/4	234	266	180	4.2
Example 2	Ce-Zr-Y-O	58/38/4	253	286	221	3.9
Example 3	Ce-Zr-Y-O	58/38/4	263	301	216	4.1
Example 4	Ce-Zr-La-Pr-O	58/32/3/7	245	270	201	4.0
Comparative Example 1	Ce-Zr-Y-O	58/38/4	280	308	242	2.5
Comparative Example 2	Ce-Zr-La-Pr-O	58/32/3/7	269	303	253	2.2
Comparative Example 3	Ce-Zr-Y-O	58/38/4	302	366	299	3.3

[0061] A cerium-zirconium composite metal oxide having improved durability at high temperature and a stable oxygen

storage capacity is provided. The cerium-zirconium composite metal oxide is characterized in that the total mole number of Ce and Zr is at least 85% based on the total mole number of metal in the composite metal oxide, a molar ratio Ce/Zr is within a range from 1/9 to 9/1, and an isoelectric point of the composite metal oxide is more than 3.5. Preferably, the molar ratio Ce/Zr is within a range from 3/7 to 7/3 and the isoelectric point is within a range from 3.8 to 5.0, and the cerium-zirconium composite metal oxide contains a rare earth metal (excluding Ce) in a concentration of less than 15% by mole based on the total mole number of metal in the composite metal oxide. Also the present invention provides a cerium-zirconium composite metal oxide, characterized in that CeO_2 forms a core surrounded by ZrO_2 .

10 **Claims**

1. A cerium-zirconium composite metal oxide, characterized in that the total mole number of Ce and Zr is at least 85% based on the total mole number of metal in the composite metal oxide, a molar ratio Ce/Zr is within a range from 1/9 to 9/1, and an isoelectric point of the composite metal oxide is more than 3.5.
- 15 2. The cerium-zirconium composite metal oxide according to claim 1, wherein the molar ratio Ce/Zr is within a range from 3/7 to 7/3 and the isoelectric point is within a range from 3.8 to 5.0.
- 20 3. The cerium-zirconium composite metal oxide according to claim 1 or 2, which contains rare earth metal (excluding Ce) in a concentration of less than 15% by mole based on the total mole number of metal in the composite metal oxide.
- 25 4. A cerium-zirconium composite metal oxide, characterized in that the total mole number of Ce and Zr is at least 85% based on the total mole number of metal in the composite metal oxide and CeO_2 forms a core surrounded by ZrO_2 .
- 30 5. The cerium-zirconium composite metal oxide according to claim 4, wherein the CeO_2 core has a diameter within a range from 5 to 20 nm.
- 35 6. An exhaust gas purifying catalyst comprising the cerium-zirconium composite metal oxide of any one of claims 1 to 5 and a noble metal supported on the cerium-zirconium composite metal oxide.
7. A method for synthesizing the cerium-zirconium composite metal oxide of any one of claims 1 to 4, which comprises mixing a ceria sol and a zirconium compound solution or a zirconia sol to prepare a suspension, and drying and firing the mixture.

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Fig.1

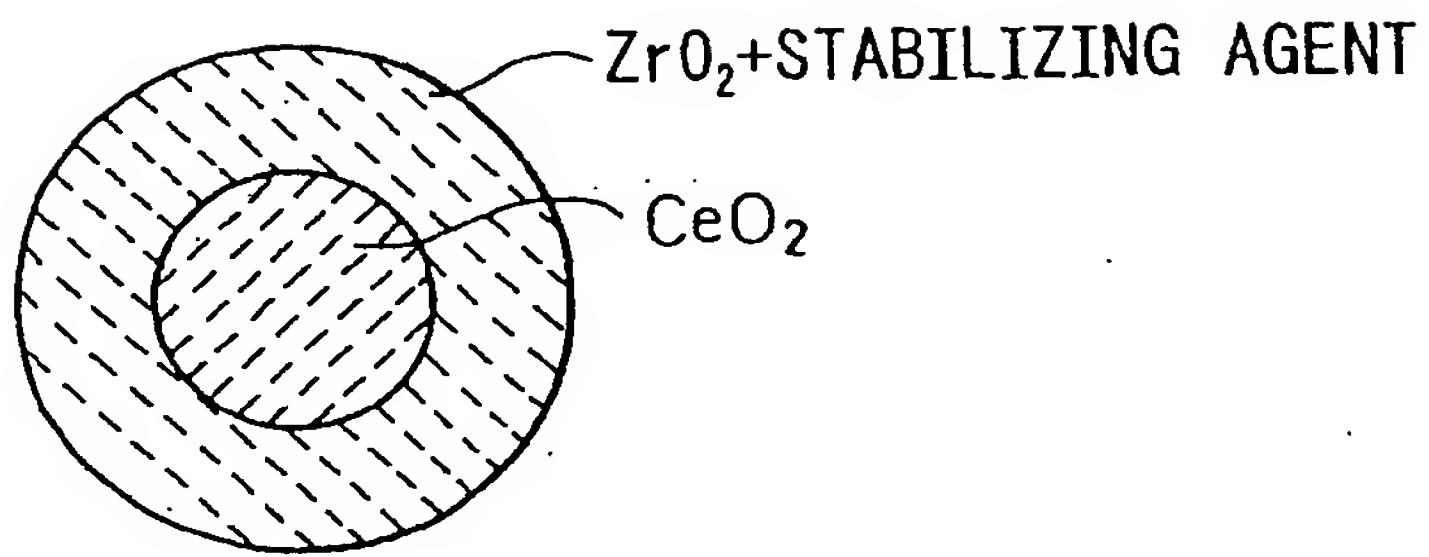
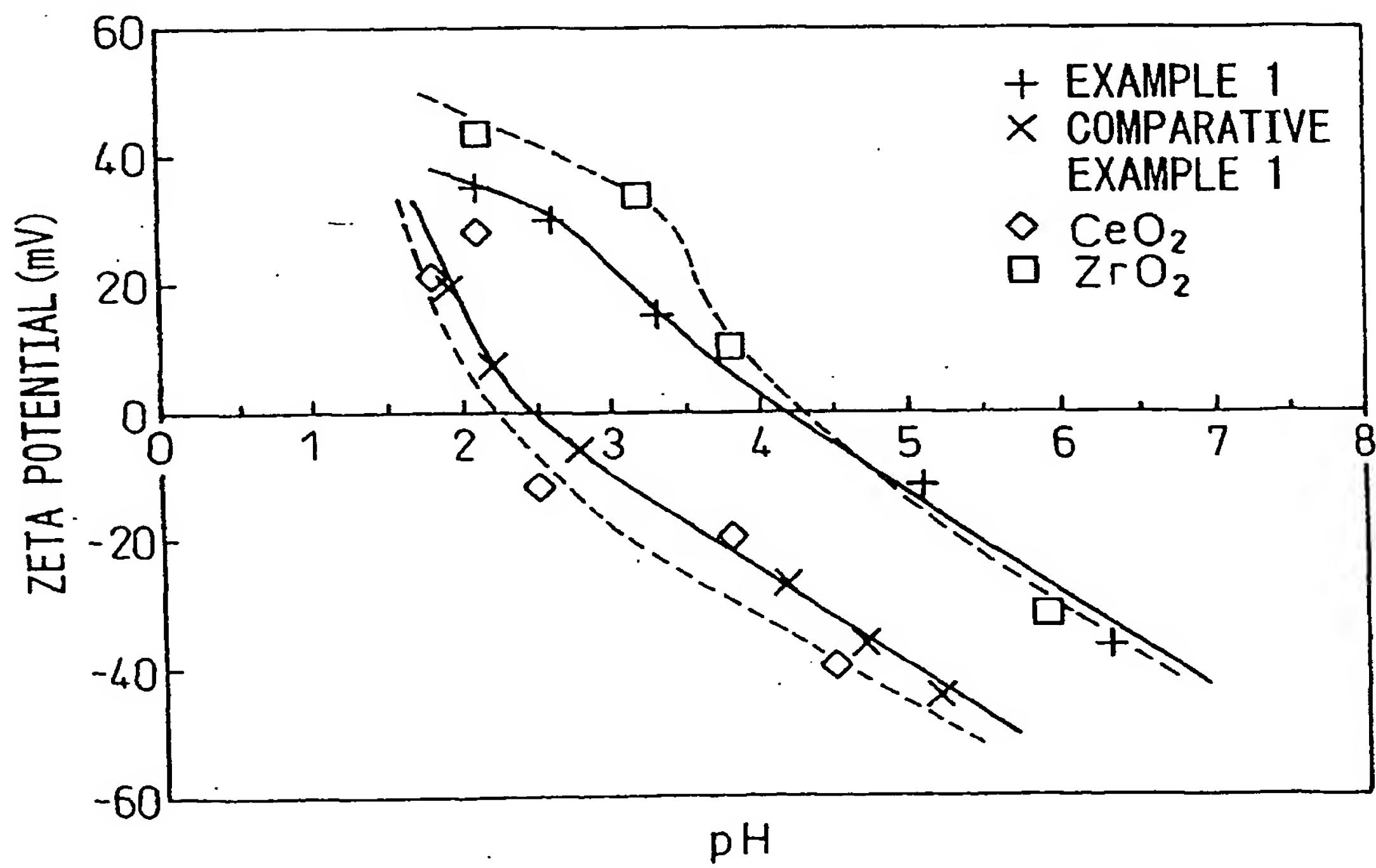


Fig.2

RELATIONSHIP BETWEEN pH AND ZETA POTENTIAL





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 03 02 0939

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 211 (C-0715), 2 May 1990 (1990-05-02) & JP 02 048418 A (CATALYSTS & CHEM IND CO LTD), 19 February 1990 (1990-02-19) * abstract * ---	1,4,5,7	C01G25/00 B01J23/10 B01J21/06
X	FR 2 756 819 A (RHONE POULENC CHIMIE) 12 June 1998 (1998-06-12) * page 2, line 13 - line 20; examples 1-3 * * page 2, line 26 - line 31 * * page 3, line 3 - line 8 * ---	1-3	
X	US 5 693 299 A (CHOPIN THIERRY ET AL) 2 December 1997 (1997-12-02) * column 4, line 14 - line 36; example 2 * * column 1, line 10 - line 55 * ---	1-3,6	
A,D	EP 0 955 267 A (ANAN KASEI CO LTD) 10 November 1999 (1999-11-10) * claims 1-9 * & JP 10 194742 A 28 July 1998 (1998-07-28) ---	1-7	TECHNICAL FIELDS SEARCHED (Int.Cl.) C01G B01J
A,D	EP 0 614 854 A (RHONE POULENC CHIMIE) 14 September 1994 (1994-09-14) * claims 1-40 * & JP 06 279027 A 4 October 1994 (1994-10-04) -----	1-7	
<p>The present search report has been drawn up for all claims</p> <p>1</p>			
<p>Place of search THE HAGUE</p>		<p>Date of completion of the search 12 March 2004</p>	Examiner Siebel, E
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>	

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 03 02 0939

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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12-03-2004

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
JP 02048418	A	19-02-1990	JP	2686103 B2	08-12-1997
FR 2756819	A	12-06-1998	FR	2756819 A1	12-06-1998
			CA	2274013 A1	11-06-1998
			CN	1244177 A	09-02-2000
			EP	0950022 A1	20-10-1999
			WO	9824726 A1	11-06-1998
			JP	2000505771 T	16-05-2000
			KR	2000057428 A	15-09-2000
			NO	992741 A	05-08-1999
			TW	426542 B	21-03-2001
			US	2002115563 A1	22-08-2002
US 5693299	A	02-12-1997	FR	2699524 A1	24-06-1994
			AT	179680 T	15-05-1999
			AU	668236 B2	26-04-1996
			AU	5234793 A	30-06-1994
			BR	9305146 A	01-11-1994
			CA	2111892 A1	22-06-1994
			DE	69324785 D1	10-06-1999
			DE	69324785 T2	02-12-1999
			DE	605274 T1	26-03-1998
			EP	0605274 A1	06-07-1994
			ES	2133372 T3	16-09-1999
			FI	935748 A	22-06-1994
			JP	2947449 B2	13-09-1999
			JP	6226094 A	16-08-1994
			KR	270153 B1	16-10-2000
			US	5712218 A	27-01-1998
			ZA	9309353 A	16-09-1994
EP 0955267	A	10-11-1999	JP	10194742 A	28-07-1998
			DE	69724655 D1	09-10-2003
			EP	0955267 A1	10-11-1999
			US	6171572 B1	09-01-2001
			CN	1241988 A ,B	19-01-2000
			WO	9829341 A1	09-07-1998
EP 0614854	A	14-09-1994	FR	2701471 A1	19-08-1994
			AT	183725 T	15-09-1999
			AU	668445 B2	02-05-1996
			AU	5392494 A	08-09-1994
			BR	9400472 A	27-09-1994
			CA	2115305 A1	11-08-1994
			DE	69420163 D1	30-09-1999
			DE	69420163 T2	20-04-2000

EPO FORM P0459
For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 03 02 0939

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
 The members are as contained in the European Patent Office EDP file on
 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-03-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0614854 A		EP 0614854 A1	14-09-1994
		EP 0930271 A2	21-07-1999
		ES 2138054 T3	01-01-2000
		FI 940595 A	11-08-1994
		JP 2787540 B2	20-08-1998
		JP 6279027 A	04-10-1994
		US 5607892 A	04-03-1997
		US 5626826 A	06-05-1997
		ZA 9400837 A	05-09-1994

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82